Studies on Mg and Mn-doped ZnO Thin Films via Spray Pyrolysis Technique

A Synopsis Submitted

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Introduction

A thin film is a layer of material having a thickness in the range of a nanometer to several micrometers. Thin films' behavior and properties are different from those of thick/bulk materials. Thin film materials show surface quality-dependent properties. Moreover, the quality of thin films can be enhanced by several techniques and modifications such as controlling thickness, doping, some surface treatments, etc. Everyday examples of thin films include soap bubbles, oil slicks on water and anti-reflection coating on eyeglasses. Thin films are used for protecting the surfaces of many materials from scratches, fingerprints and even corrosion.

Zinc oxide (ZnO), is a representative of II-VI groups and an n-type metal oxide semiconductor compound that is highly durable and heat resistant. Zinc oxide has a hexagonal wurtzite structure [1]. It is a very versatile and thermodynamically stable material at an ambient temperature. Also, ZnO is a unique semiconducting oxide due to its piezoelectric and transparent conducting properties [2]. It has high electrical conductivity and optical transmittance in the visible region. ZnO has a wide band gap (3.37eV) and a large exciton binding energy (60 meV) [3]. These properties make it applicable for photo catalytic activities. ZnO is an important candidate for thin film technology due to its wide applications such as photodetectors [4], solar cells, biosensors, gas sensors and spintronic devices. ZnO nanostructures are in huge demand as they are widely been used in industries and laboratories due to their applicability in UV-filtering, catalytic, antibacterial properties. Recently, ZnO nanomaterials are preferred for UV-resistant additives.

Nano structured thin films on the other hand have some scientific importance from a research point of view. They can be broadly studied on the basis of their structural impact and functionality. Fabricating better quality ZnO nanostructures has become interesting and crucial. Experimental results are often dependent on synthesis methods. Several deposition techniques were used for the preparation of doped ZnO thin films such as laser deposition, sol-gel, DC-magnetron sputtering, chemical vapor deposition, electrodeposition, wet chemical route and spray pyrolysis [5].

Furthermore, in some environmental conditions, ZnO seems to be slightly unstable. This condition can be tackled by doping ZnO with some suitable dopant. Doping of different metals

like Mn, Mg, Ce, Fe, Ga and Al in ZnO helps to engineer the band gap. Especially, magnesium (Mg) doping in ZnO has a higher influence on its crystallite size, shape, band gap and conductivity. Also, Manganese has ionic radii (0.66Å) which is close to the ionic radii of Zinc (0.60 Å) that making it suitable material as a dopant for zinc oxide. Adding Mn^{+2} in the ZnO lattice avoids segregation and results in effortless solubility. Doping ZnO with Mg and Mn enhances optoelectronic applications like solar cells, light-emitting diodes, photodetectors, ultraviolet laser diodes, gas sensing applications.

The Spray Pyrolysis technique has some advantages compared to other methods. It is a comparatively simple, inexpensive, laboratory friendly, easy control of stoichiometry and gives films with uniform thickness. It has high stability and transparency in the visible region.

Literature Review:

- **Y. Bouachiba et al. [6], in their work of Optoelectronic and birefringence properties of weakly Mg-doped ZnO thin films prepared by spray pyrolysis,** concluded that the undoped thin film had a multi-sized grain distribution, meanwhile, the $Mg_{0.05}Zn_{0.95}O$ had a more homogeneous grain distribution. Mg doping in the ZnO films led to a blue shift of the optical band-gap energy and a depletion of the conduction band due to the drop in free carriers' density that had a direct effect on the ordinary and the extraordinary refractive indices that were found to decrease.
- **M. Biswas et al. [7] in his study on Structural and Optical Characterization of Magnesium doped Zinc Oxide Thin Films Deposited by Spray Pyrolysis** showed that the Optical band gap increased from 3.24ev to 3.46eV with the increase of Mg concentration from 0 to 40%. Transmittance and refractive index of the Mg-doped ZnO thin films decreased due to the increase of Mg concentration. The EDX spectra confirmed the increase of Mg and consequent reduction in Zn content in the Mg-doped ZnO thin films.
- **S.Goudarzi et al. [8] in their work on "Role of substrate temperature on the ammonia gas sensing performance of Mg-doped ZnO thin films deposited by spray pyrolysis technique: application in breath analysis devices",** showed that the

Mg doped ZnO thin films are a good candidate for ammonia gas sensing properties at the temperature 375° C.

- **M. Rochdi et al. [9] in their study on the synthesis and characterization of Mg-doped ZnO thin Films** showed that the transmittance of MZO thin films increased from 75 to about 90% and optical band gap energy from 3.20 to 3.43 (eV).
- **A.J. Kulandaisamy et al. [10] on room temperature ammonia sensing properties of ZnO thin films grown by spray pyrolysis: effect of Mg doping** revealed that all the films were polycrystalline in nature with the hexagonal wurtzite crystal structure. Spherical shaped uniformly distributed grains were observed for all the films with a slight change in size. The optical absorption edge shifted towards the lower wavelength with an increase in Mg-dopant concentration which confirmed the blue shift. Films with lower Mg-dopant concentration showed maximum response towards ammonia at room temperature with quick response and recovery times.
- **P. Singh et al. [11] in their work on "Mn-doped ZnO nanocrystalline thin films prepared by ultrasonic spray pyrolysis"** observed the structural and optical properties of the films and elucidated that the Mn^{2+} ions have substituted the Zn^{2+} ion without changing the wurtzite structure of ZnO. The value of the band gap was found to decrease from 3.24 eV to 3.14 eV with a corresponding increase in Mn concentration. The observed decrease in the band gap with an increase in doping concentration was explained in terms of sp–d exchange interaction.
- **A. Lopez-Suarez et al. [12] in their study on the optical, structural and electrical properties of ZnO thin films doped with Mn,** show that lattice constants, crystallite size and resistivity increase with Mn doping. On the other hand, energy band gap values decrease when the samples were doped with Mn, due to the s–d and p–d exchange interactions
- **B. Singh et al. [13] in "Effects of Mn Doping on Zinc Oxide Films Prepared by Spray Pyrolysis Technique",** depicted that the optical measurement shows the shift in absorption edge of Mn-doped ZnO films towards the longer wavelength side. The optical band gap goes down, whereas the refractive index increases with dopant concentration.

- **T.Elavarasan et al. [14] in "Spray deposited nanostructured ZnO: Mn thin films for ammonia vapour sensing application"** studied that the band gap decreased from 3.39 eV to 3.22 eV with increased mn doping which is good for the ammonia sensing.
- **D. E. Motaung et. al. [15] on defect-induced magnetism in undoped and Mn-doped wide band gap zinc oxide grown by aerosol spray pyrolysis** performed surface morphology analysis and revealed that incorporation of Mn in the ZnO matrix results in the formation of "doughnut-like" structures while the corresponding un-doped ZnO showed permeable structures only at long deposition time.

From the above Review of Literature we have concluded that there is an influence of Mg and Mn doping on the structural, morphological and optical properties of pure ZnO thin films. Also the gas sensing characteristics of pure ZnO thin films enhanced with Mg and Mn doping.

Motivation for the Present Work:

- Fabrication of doped ZnO, has become interesting and crucial.
- ZnO thin films offer a variety of applications in integrated piezoelectric, optics, transparent electrodes and Light Emitting Diodes (LEDs).
- The transparent conducting oxide (TCO) materials have received much attention because of their physical properties. Zinc oxide (ZnO) is one of them.
- ZnO is considered a good candidate for optoelectronic applications in the near UV region and for transparent electronics, ranging from the light-emitting diode, laser diodes, gas sensors and solar cells.
- Doping is the addition of another atom into an element or compound by purpose in order to improve or to modify the properties of the compound or element. In this semiconductor technology, doping and crystal defect are combined in order to control electrical conductivity, optical property, magnetic property and other physical properties.
- The addition metal-doped into ZnO precursor solution will control the synthesis process systematically. In order to improve the ZnO physical properties such as optical and electrical properties it is common to dope with metals from group IIIA periodic table such as B, Al, Mg, Ca, Cd, and Ga.

The objective of the present Work:

- The objective of the present work is to synthesize the Undoped, Mg-doped and Mn-doped ZnO Thin Films by Spray Pyrolysis Method.
- To study the effect of Mg and Mn doping on structural, morphological, optical and gas sensing properties of ZnO thin Films.

Methodology:

- Undoped, Mg doped and Mn doped ZnO thin films will be synthesized by spray pyrolysis method.
- Spray pyrolysis is very efficient, cost-effective and utilizes simple equipment.
- Spray pyrolysis is a process in which a thin film is deposited by spraying a solution on a heated surface, where the constituents react to form a chemical compound.
- The Spray Pyrolysis (SP) technique has some advantages compared to other methods. It is simple and non-expensive. It has high stability and transparency in the visible long waves region.
- This technique offers considerable preparative parameters to control airflow, spray rate, adherence of substrates, solution concentration, droplet size, volume, the gap between the substrate and spray gun for the desired SPs.

Characterizations:

1. Structural Characterization:

X-Ray Diffraction:

The Powder X-Ray Diffraction pattern will be recorded for Undoped, Mg-doped and Mn doped ZnO Thin Films. The lattice constant, crystal structure, grain size and film thickness of the prepared samples will be studied.

2. Morphological characterization:

- **Scanning Electron Microscopy (SEM)**

The surface morphology of the prepared samples will be studied by SEM.

- **Energy Dispersive X-Ray Analysis (EDAX)**

The compositional analysis of the prepared samples will be studied by EDAX.

3. Optical Properties

- **UV-Visible Spectrophotometer**

Synthesized samples of Undoped, Mg-doped and Mn doped ZnO thin films will be characterized from UV-Visible Spectrophotometer by calculating the energy band gap of the prepared samples.

4. Gas sensing properties will be studied.

Year Wise Plan of Work and targets to be achieved:

First Year:

- Course work
- Literature Review
- Preparation of Mg-doped ZnO Thin Films from Spray Pyrolysis Method.
- Structural, Morphological, Optical and Gas Sensing characterizations.
- Paper Publication on the work.

Second Year:

- Preparation of Mn-doped ZnO Thin Films from Spray Pyrolysis Method.
- Structural, Morphological, Optical and Gas Sensing characterizations.
- Paper Publication on the work.

Third year:

- Data analysis and the results obtained will be communicated to the respective journals for publication.
- Submission of the thesis for the Doctoral degree.

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